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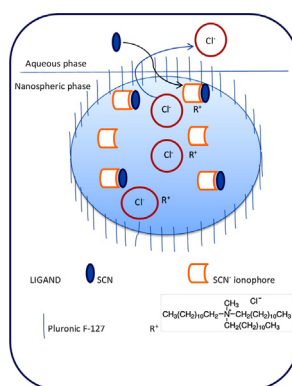
## Development of ionophore-based nanosphere emulsion incorporating ion-exchanger for complexometric titration of thiocyanate anion



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## GRAPHICAL ABSTRACT



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## ABSTRACT

Ionophore-based ion-exchange nanosphere emulsion was prepared and tested for the determination of thiocyanate. The emulsified nanosphere contained the cationic additive tridodecylmethyl ammonium chloride (TDMAC), the plasticizer, and the ionophore Mn(III)-salophen or Mn(III)-salen. This emulsion was used as titrating agent for thiocyanate complexation with ionophores, which could be transduced using an ion-selective electrode (ISE) as an indicator electrode for the end point detection. The method showed no need for pH control and reliable selectivity, as thiocyanate could be determined in presence of other interfering ions with high accuracy. As well, the emulsion was stable and could be used for approximately couple of weeks. The developed emulsion could be used for the determination of thiocyanate in human saliva with standard deviation <4%. In sum, the proposed method could be used as an alternative for the argentometric titration and would open new avenues for the determination of neutral, anionic, and cationic species without necessity for water soluble ligands or pH control.

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## Introduction

Complexometric titration is a classic method that could be used for the determination of plethora of metal cations using different ligands or chelating agents [1]. These ligands form so stable complexes with the metal cations and the end point can be detected easily using visual indicators. However, the absence of the suitable chelating agent that can form stable complex with anionic species

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limits the application of this valuable method for anion determination [1]. Argentometric titrations could overcome this problem using different methods (Mohr, Fajan and Volhard) [2]. However, these methods still suffer from the limited applicability to certain number of anions (halides, cyanide, phosphate, sulphide, and thiocyanate), the necessity for pH control, and formation of the precipitate that may hinder the visual detection of the end point [2].

On the other hand, ion-selective electrodes (ISEs) are one of the simplest instrumental techniques that offer several benefits, such as low cost, short response time, ease of construction, high selectivity, and on-line monitoring [3]. The most important component of the ISE is the ionophore that controls the selectivity of electrode via molecular recognition between the ionophore and the analyte [3,4]. So far, very large numbers of ionophores were used for the determination of the different anionic species [3–6] to overcome the problem of complexometric titrations. Potentiometric titration is a derivative of ISEs that could be applied for the determination of different species [6,7], easy to perform, cost-effective, and applicable when used in turbid solutions.

The advantages of complexometric titration, ISEs, and potentiometric titration could be joined in a powerful technique named complexometric titration using ionophore-based ion-exchange emulsion. This method was first reported by Zhai et al. for the determination of metal cations,  $Pb^{2+}$ , and  $Ca^{2+}$ , using ionophore-based nanosphere emulsion [8]. The aqueous analyte concentrations of  $Pb^{2+}$  or  $Ca^{2+}$  were titrated against ionophore-based ion-exchange emulsions as titrant. The lipophilic ion-exchanger extracted the analyte ions from the aqueous phase to the lipophilic nanosphere phase to be complexed by the specific ionophore. This depletion in the concentration of the aqueous cation caused a decrease in the potential reading of the indicator electrode. The amount of extracted ions was controlled by the ion-exchanger amount, where the ionophore was responsible for controlling selectivity [8]. Schwarzenbach conditions for complexometric titration were satisfactory, as the small size of the nanosphere <100 nm, ensures rapid complexation reaction between ionophore and analyte ion with definite stoichiometry and high formation constant [2,3]. Later, the same group could apply this method for the determination of perchlorate [9]. However, this work lacked the selectivity as the emulsion was only ion-exchanger based.

Therefore, this work was designed to report the use of ionophore-based ion-exchange emulsion for the determination of an anion, thiocyanate. This enable us to move the complexometric titration from the homogenous aqueous phase to the heterogenous aqueous/organic phases, which allow the possibility of complexing different anions by different ionophores. Thiocyanate was taken as an example, where this approach can be applied for the different anions using the suitable ionophore.

## Experimental

### Reagents and solutions

All chemicals were of analytical grade. Pluronic F-127 (F127), 2-nitrophenyl octyl ether (o-NPOE), tetrahydrofuran (THF), sodium tetrakis-[3,5-bis(trifluoromethyl)phenyl] borate (NaTFPB), tridodecylmethylammonium chloride (TDMAC), Mn(III)-salen (Fig. 1), and high molecular weight poly (vinyl-chloride) (PVC) ( $M_w = 43,000$ ) were obtained from Sigma-Aldrich (Munich, Germany). Potassium thiocyanate (KSCN), Silver nitrate ( $AgNO_3$ ), glacial acetic acid, and sodium acetate were obtained from ADWIC (Cairo, Egypt). Mn(III)-salophen ionophore (Fig. 1) was prepared as reported before [6].

Double distilled water was used throughout the experimental work for the preparation of the buffer and different solutions.  $10^{-1} \text{ mol L}^{-1}$  KSCN or KI stock solutions were prepared by dissolving the exact weight in double distilled water and the lower concentration solutions were prepared by appropriate dilutions. Acetate buffer was prepared as described elsewhere [10,11]. Briefly,  $5.0 \times 10^{-2} \text{ mol L}^{-1}$  sodium acetate was prepared by dissolving the exact weight in 240 mL double distilled water followed by addition of drops of glacial acetic acid to adjust the pH at 4.5 and mass up with water to 250 mL. This buffer could be used later for the preparation of thiocyanate solutions.

Saliva samples were collected from a healthy person (corresponding author) and treated as reported before [6]. The collected saliva samples (two) transferred to centrifugation tubes and centrifugated at 6000 rpm for ten min. From the resulting clear solutions, volume of 250  $\mu\text{L}$  was pipetted into a 25 mL volumetric flask. This solution was used in titration against Mn(III)-salophen-based emulsion for the determination of its thiocyanate content; the experiment was repeated thrice. The results were compared with that obtained from the potentiometry using ISE [6]. Different amounts of  $SCN^-$  and 1 mL urine of the corresponding author were transferred to 25 mL measuring flask and adjusted to the mark with water [5]. These solutions were subjected to the potentiometric titration using Mn(III)-salophen emulsion and experiment was repeated three times.

### Preparation of thiocyanate-selective emulsion

For Mn(III)-salophen-based emulsion, 2.24 mg of ionophore, 1.24 mg of TDMAC (68% (mole ratio of ion-exchanger/ionophore)), 8.0 mg of o-NPOE, and 3.0 mg of F127 were dissolved in 2.0 mL of THF to form a homogeneous solution. Aliquot of 0.5 mL THF solution was pipetted and 3 mL double distilled water was injected, then vortexing at 1000 rpm. Compressed air was blown on the surface for 30 min to remove THF. For Mn(III)-salen emulsion, 10.3 mg of the ionophore, 0.63 mg of TDMAC (6.8% (mole ratio of ion-exchanger/ionophore)), 6.08 mg of o-NPOE, and 2.48 mg of F127 were dissolved in 2.0 mL of THF, followed by the same procedures above [8,9].

### Membranes and electrodes

The thiocyanate-selective membrane was prepared by dissolving the mixture composed of 16.5 mmol  $\text{kg}^{-1}$  ionophore, 6.9 mmol  $\text{kg}^{-1}$  NaTFPB, 63.1 wt% o-NPOE, and 33.5 wt% PVC in 1.5 mL THF. The cocktail solution was then poured into a glass ring (22 mm in diameter) placed on a glass slide and dried overnight at room temperature under a dust-free environment. Proper part of the membrane was punched and glued to a polished end of a PVC tube using PVC/THF slurry. An inner filling solution of  $10^{-2} \text{ mol L}^{-1}$  thiocyanate was used and then the electrodes were conditioned for 24 h in the same solution, pending uses as an indicator electrode [6].

### Instrumentations and measurements

For potentiometric titrations, ionophore-based emulsions as titrating agents were titrated against  $4.0 \times 10^{-5}$ ,  $1.0 \times 10^{-5}$ , and  $1.0 \times 10^{-4} \text{ mol L}^{-1}$  KSCN aqueous and buffered analytes, and the thiocyanate-selective electrode as endpoint detector. In case of selectivity measurement, the analyte solution contained  $2.5 \times 10^{-5} \text{ mol L}^{-1} SCN^-$  and  $1.1 \times 10^{-5} \text{ mol L}^{-1} I^-$  was titrated against Mn(III)-salophen titrant.

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